

HYDROGEN FROM NATURAL GAS FOR FUEL CELLS

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INTRODUCTION

To be practical, any commercial fuel cell system for use with natural gas must be competitive with existing power generation schemes. Under this stringent economic limitation, many potential fuel cell systems are eliminated. A review of the more common fuel cells (Table 1) summarizes the authors' estimate of these systems, based only on the criterion of economic feasibility for use in the gas industry.

At the beginning of 1963, a low-temperature fuel cell program was initiated at the Institute of Gas Technology to study the use of reformed natural gas and air in acid fuel cells. This system, based on the use of impure hydrogen, does not appear to have been extensively studied elsewhere. The following considerations motivated this course of study:

1. Natural gas (methane) is difficult to react directly at low temperatures in fuel cells.
2. Hydrogen is known to be a good fuel cell fuel at low temperatures.
3. Natural gas is an easily reformed hydrocarbon fuel.
4. Reformed natural gas will contain about 80 mole percent hydrogen.
5. An acid cell, in principle, does not require a high-purity hydrogen feed.

The present paper is concerned with that portion of the IGT program devoted to the production from natural gas of a hydrogen-rich feed which is compatible with economic fuel cell operation.

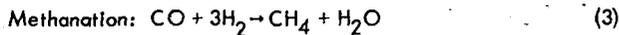
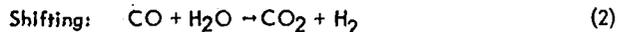
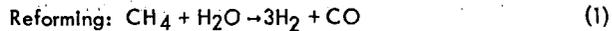
The objectives set forth for the hydrogen generation system were dictated by economic as well as practical feasibility. The project was guided by the following goals:

1. Low-cost components.
2. Maximum methane conversion.
3. Minimum carbon monoxide content.
4. No moving parts.
5. Low system pressure drop.

The need for low-cost components with low pressure drop eliminated conventional palladium diffuser purification schemes. The impracticability of having moving parts in small generators (delivering 2- to 100-kilowatt fuel cells) eliminated scrubbing towers, often used in larger hydrogen purification processes. Maximum methane conversion is essential to obtain high efficiency. The desirability of a low carbon monoxide concentration resulted from information derived from the fuel cell portion of the program. All of the above goals are based on the needs of on-site generation systems for use in the gas industry.

THE HYDROGEN GENERATION SYSTEM

To achieve the design goals outlined above, a multi-stage process was necessary. The scheme studied was a three-stage process made up of the following steps:



The overall process is shown schematically in Figure 1.

Methane Reforming

Reaction (1) being well-known, it was the intent of this study to establish operating parameters which might be useful in the construction of small hydrogen generators. Experiments were conducted in reactors capable of providing power for a fuel cell system of a few hundred watts. Since most experience with these reactions is with larger systems, it was felt that scaleup in this instance would be relatively straightforward.

A steel reactor 1 inch in diameter and 18 inches long was filled to a 4-inch bed height with Girdler G-56B catalyst, which was reduced in size to give a reactor diameter-to-particle size ratio of about 10:1. The total pressure drop through the reactor at a space velocity of 1000 SCF per cu. ft. of catalyst per hour was only 1 inch of water. A steam-to-methane mole ratio of 3:1 was chosen, and studies were made at space velocities of 500 and 1000 SCF per cu. ft. of catalyst per hour at a variety of temperatures. Effluent gas was analyzed chromatographically for carbon monoxide and methane with a Fisher-Gulf partitioner using a charcoal column. The only other detectable carbon-containing species present, carbon dioxide, was determined from a mass balance.

The results of these experiments (Figure 2) show that methane conversion was a strong function of space velocity with respect to the temperature required to achieve complete conversion, higher temperature being required for higher space velocities. For the space velocities studied, complete conversion was obtained at 800°C. and above. The exit gas carbon monoxide content was not a strong function of space velocity, and the effluent carbon monoxide concentration at 800°C. was about 15 mole %. At the lower space velocity, experiments conducted at temperatures up to 1000°C. resulted in a further increase in carbon monoxide concentration. Since the ultimate goal is a low carbon monoxide content in the fuel cell feed gas, operating at this high temperature is undesirable. Also, from a thermal efficiency standpoint the lowest possible reforming temperature is most desirable. Having established reasonable operating limits for the reforming stage, the effluent from the reformer was used as the input to the shift reactor.

Carbon Monoxide Shift

Conventional shift processes operating between 300° and 500°C. require, to achieve a low carbon monoxide content (3000 parts per million or less), the use of a carbon dioxide absorption stage, which is unwieldy for use in small systems. Recently work done by Moe (1) indicated that reformed and shifted gases containing 2000 to 3000 parts per million carbon monoxide could be achieved without carbon dioxide removal if a low-temperature (175° to 300°C.) shift catalyst was used. This relatively new catalyst, Girdler G-66, was placed in a reactor of 1-inch diameter and 18-inch length, filled to a bed height of 8 inches, and the shift reaction was studied with respect to temperature, space velocity, and

steam-to-gas ratio. As in the study of the reforming reaction, the carbon monoxide and methane contents of the effluent gas stream were analyzed chromatographically.

The results of this study are shown in Figures 3 and 4. In Figure 3, the effects of space velocity and temperature on the carbon monoxide content of the effluent gas are indicated. At the higher space velocity, 1000 SCF per cu. ft. of catalyst per hour, the desired reduction in the carbon monoxide content of the effluent gas could not be obtained. Experiments at still higher space velocities, 2000 SCF per cu. ft. of catalyst per hour, yielded much poorer results, not reported here. However, at a space velocity of 500 SCF per cu. ft. of catalyst per hour, a minimum in the carbon monoxide concentration is seen to occur at about 267°C. In Figure 4, the strong effect of the steam content of the reacting mixture on the effluent carbon monoxide concentration is indicated. At 250°C., a continuous reduction in the carbon monoxide content is obtained as the steam-to-methane ratio is increased. The maximum ratio tested was 7.3:1, as this ratio readily yielded a carbon monoxide content which was known to be further reducible by methanation. Whether additional steam is desirable will be decided later on the basis of the cost of the steam, as well as the fuel cell performance on impure hydrogen feed.

Carbon Monoxide Methanation

Reaction 3, methanation, posed the greatest challenge in the overall carbon monoxide reduction process. The first attempts at achieving an effective reduction in the carbon monoxide content of a synthetic gas containing 80 mole % hydrogen, 19.7 mole % carbon dioxide, and 0.3 mole % carbon monoxide, using conventional methanation catalysis, were unsuccessful. Either of two events occurred. At very low temperatures no reactions occurred, while at higher temperatures the water gas shift was promoted along with methanation and at best only a slight decrease, and in some cases an actual increase, in carbon monoxide was observed.

The problem was to find a catalyst which would permit selective methanation of carbon monoxide in the presence of carbon dioxide, under conditions in which the latter is present in concentrations two orders of magnitude greater than the former. The need for selective methanation is twofold. If appreciable amounts of the carbon dioxide react, the exothermic nature of the reaction almost ensures a complete loss of temperature control in the system. As the temperature rises, more carbon dioxide is methanated and large amounts of hydrogen are consumed. In the limiting case, all of the hydrogen and carbon dioxide could react to form methane. Equilibrium calculations clearly indicated the desirability of low-temperature operation, although even under these conditions the sought-after reduction did not appear achievable.

Using the above-mentioned gas composition, experiments were conducted with a ruthenium-on-alumina catalyst obtained from Englehard Industries, Inc. The effluent gas composition was analyzed with the afore-mentioned chromatograph and a Mine Safety Appliances Co. Lira Infrared analyzer. With the infrared analyzer, carbon monoxide was determined with an accuracy of about 10 parts per million. Again, a variety of parameters were studied, including excess water, and the results are shown in Figures 5 and 6. The excess water tests were made to ascertain at what stage in the hydrogen generation system it would be most favorable to remove water.

In Figure 5, the carbon monoxide content of the exit gas is seen as a function of temperature for the case of 2 mole % water vapor in the feed. Distinct minimums in carbon monoxide content – about 100 parts per million, dependent on space velocity and temperature – are seen. It is interesting that, for increasing space velocity, the same minimum carbon monoxide content is obtained, but at higher temperatures. In Figure 6, the same parameters are studied with a feed gas containing 15% water vapor. Again, the same minimum carbon monoxide concentration is obtained, but at slightly higher temperatures. It was also observed that, in the range of minimum carbon monoxide content, no appreciable conversion of carbon dioxide to methane occurred; hence, the reaction can be considered highly selective. The carbon monoxide reduction process is summarized in Figure 7.

After completing the experimental work on the reactions described above, reforming, shift, and methanation reactors were connected in series, and the complete system was analyzed. A natural gas containing about 95% methane and 5% higher hydrocarbons was passed through a sulfur removal cartridge and fed to the first reactor stage, where it was reformed in the presence of excess steam (steam-to-gas mole ratio of 7.3:1) at a space velocity of 250 SCF per cu. ft. of catalyst per hour at 800°C. The effluent from this reactor was fed to the shift reactor operating at a space velocity of 500 SCF per cu. ft. of catalyst per hour at 270°C. The effluent from this stage was fed to a condenser where a portion of the excess water was removed, and the remaining gas mixture was fed to the methanation reactor operated at a space velocity of 1000 SCF per cu. ft. of catalyst per hour and at a temperature of 190°C. The total system pressure drop was 4 inches of water column. The product gas was analyzed to be 78 mole % hydrogen, 19.7 mole % carbon dioxide, 0.3 mole % methane, 2 mole % water, and 8 parts per million carbon monoxide. The carbon monoxide was analyzed on a special MSA Lira Infrared analyzer with a sensitivity of 2 parts per million.

The tenfold improvement in performance compared with the previous experiment is not readily explainable. Some improvement had been anticipated on the basis that the original methanation experiments were performed with a feed gas containing about 3400 parts per million carbon monoxide, while the actual shift reaction reduced that concentration by almost a factor of 2. Experiments are being continued to study further the effects of steam-to-methane ratio, space velocity, and catalyst life. Experimental evidence from the fuel cell portion of the program indicates that the above-mentioned carbon monoxide content can be readily tolerated by the hydrogen electrode.

EFFICIENCY AND ECONOMICS

One of the most attractive features of fuel cells is their potentially high efficiency. When an additional processing stage, such as the one just described, is added to the fuel cell system, a reduction in overall efficiency may be anticipated. To place the external reformer-fuel cell system in the proper perspective, estimates of the overall system efficiencies have been made, based on several fuel cell and reforming parameters.

Two models have been chosen for evaluation, and these are shown schematically in Figure 8. In both schemes, it is assumed that the heat required to sustain the reforming reaction is supplied from an external burner (i.e., there is no partial combustion in the reformer). Also, both schemes assume single-pass conversion in the fuel cell.

The two schemes chosen for analysis differ only in the effect of recovery of the heat value of recycled spent fuel from the fuel cell. The following parameters have been defined:

- η_O - overall efficiency, electrical energy output based on the heat of combustion of the total amount of methane consumed
- η_V - voltage efficiency, fraction of the theoretical fuel cell potential actually obtained
- η_C - conversion efficiency, fraction of the fuel converted in the fuel cell
- η_R - reactor thermal efficiency, total reformer heat requirement, based on the assumption of nonideal insulation
- η_E - heat exchanger efficiency, fraction of heat recovered in heat exchangers

A partial summary of the results of these calculations is shown in Figures 9 and 10. In Figure 9, a case where reactor thermal efficiency is 80% was analyzed for the no-recycle system. A number of arbitrary conversions and voltage efficiencies were chosen as parameters, and the overall system efficiency was calculated as a function of heat exchanger efficiency. A typical 1-kilowatt fuel cell system using impure hydrogen feed might be expected to operate in the grey zone shown in Figure 9. An overall system efficiency range of from 21.5% to 32.5% can be realistically anticipated. For the case of a pure hydrogen cell, a somewhat higher conversion efficiency and voltage efficiency might be

anticipated, and a total system efficiency of 40% is most likely. In Figure 10, using the same parameters for the recycle schemes two characteristics are seen. First, the overall system efficiency is less dependent on conversion efficiency because of the utilization of the heating value of the spent fuel. Second, a cutoff point is seen at high heat exchange efficiency and the lowest chosen conversion efficiency. This point indicates the case where the hydrogen generation system can be operated solely on the spent fuel from the fuel cell. With the same range of heat exchanger efficiency as in the no-recycle case, an overall efficiency between 26.5% and 35.5% appears likely.

A more complete analysis of low-temperature fuel cell systems with external reforming places the parameters studied in the following order of importance with respect to overall efficiency in a recycle system operating below the cutoff point: 1) voltage efficiency, 2) reactor thermal efficiency, 3) heat exchange efficiency, and 4) conversion efficiency.

The complete economics of the present hydrogen generation system will not be known until more hardware is developed. Present estimates, based on the fuel requirements of the fuel cells under study and the catalysts and conditions described in this paper, indicate the cost of catalysts in the IGT hydrogen generation system would be less than 5 cents per watt.

REFERENCE

1. Moe, J. M., Paper presented at 145th National Meeting, Division of Petroleum Chemistry, American Chemical Society, New York, N.Y., September 8-13, 1963, Preprint No. 4-B, Vol. 8, B-29.

ACKNOWLEDGMENT

The authors wish to thank the Southern California Gas Co., the Southern Counties Gas Co., and Con-Gas Service Corp., who are sponsoring the low-temperature fuel cell project for which this investigation was made. Also, the authors wish to thank Henry Linden of IGT for his helpful suggestions with respect to the conception of the overall process and Jack Huebler of IGT for his suggestions with respect to the choice of catalysts to be used in these studies.

Table I.-STATUS OF FUEL CELLS FOR USE IN GAS INDUSTRY APPLICATIONS

<u>Type of Fuel Cell</u>	<u>Present Principal Drawback</u>	<u>Potential Gas Industry Applications</u>
Low-Temperature Alkaline Direct (25°-250°C.)	Electrolyte Incompatible with Methane	Poor
Low-Temperature Alkaline Indirect (25°-250°C.)	Cost and Technical Drawbacks of Ultra-Pure Hydrogen Production	Fair
Low-Temperature Acid Direct (25°-200°C.)	Very High Cost of Fuel Cell Catalysts and Components	Fair
Low-Temperature Acid Indirect (25°-90°C.)	High Cost of Fuel Cell Components	Good
High-Temperature Molten Salt (450°-800°C.)	Operating Lifetime	Good
High-Temperature Solid Oxide (1000°-1200°C.)	Operating Lifetime	Good

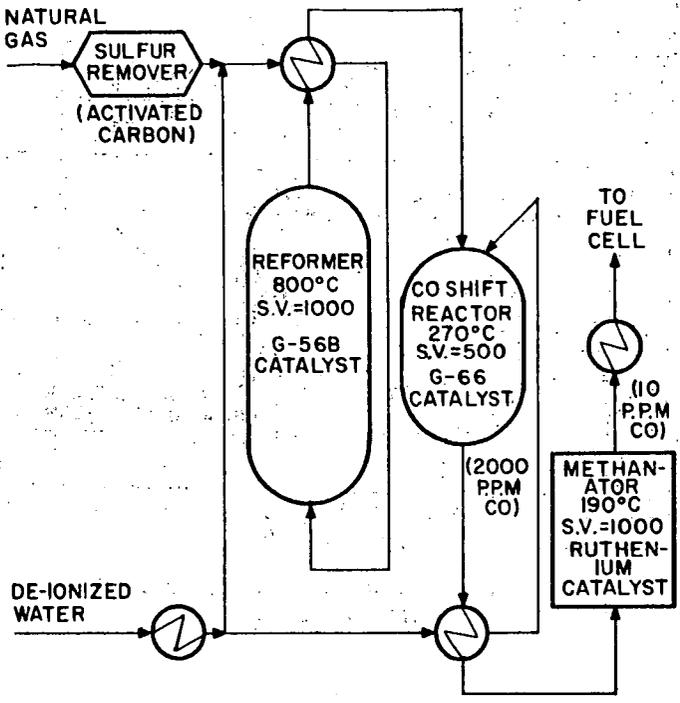


Fig. 1.-IGT HYDROGEN-GENERATION PROCESS

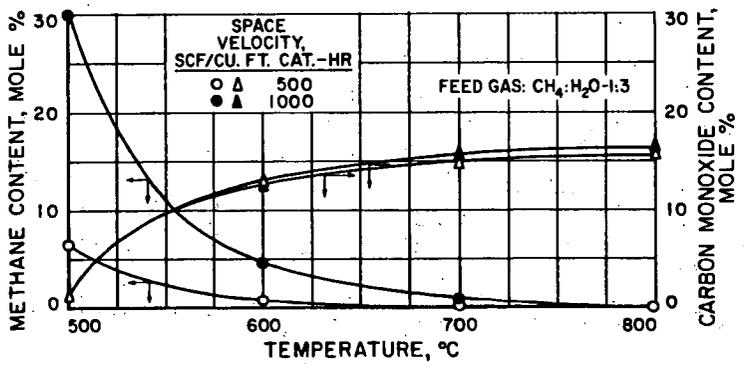


Fig. 2.-METHANE CONVERSION AND CARBON MONOXIDE COMPOSITION IN REFORMER

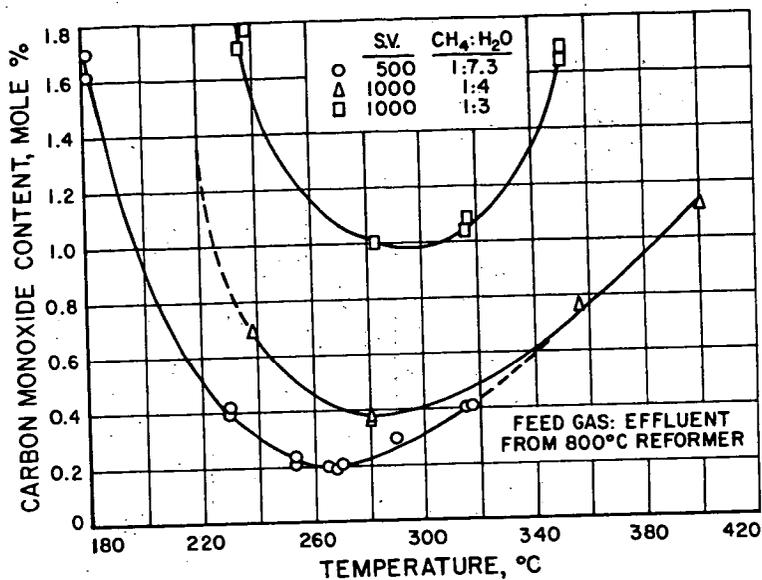


Fig. 3.-CARBON MONOXIDE CONVERSION IN SHIFT REACTOR

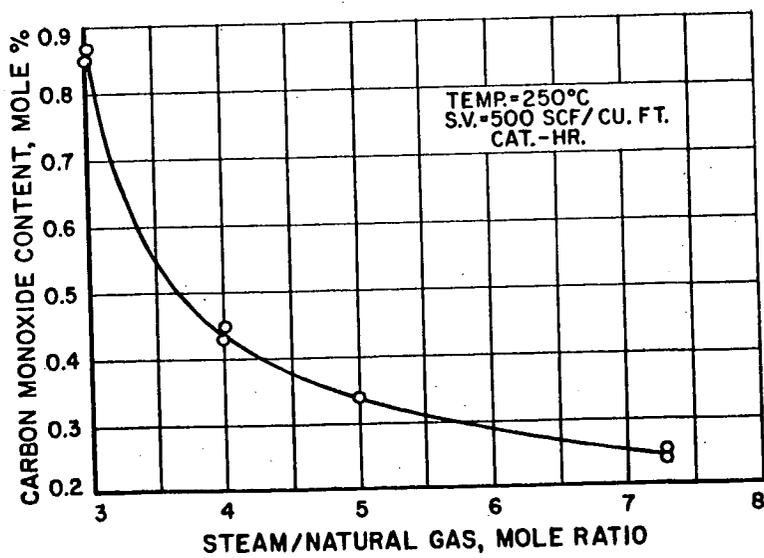


Fig. 4.-EFFECT OF STEAM-NATURAL GAS RATIO ON THE SHIFT REACTION

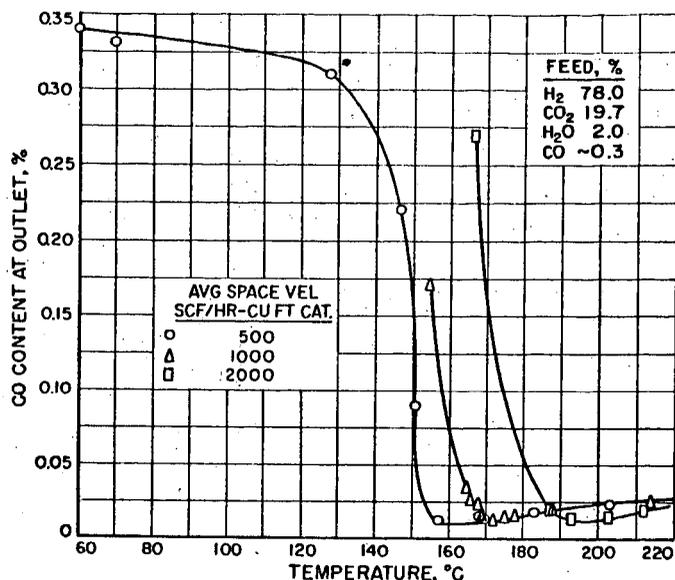


Fig. 5.-SELECTIVE METHANATION OF CARBON MONOXIDE AT LOW WATER CONTENT

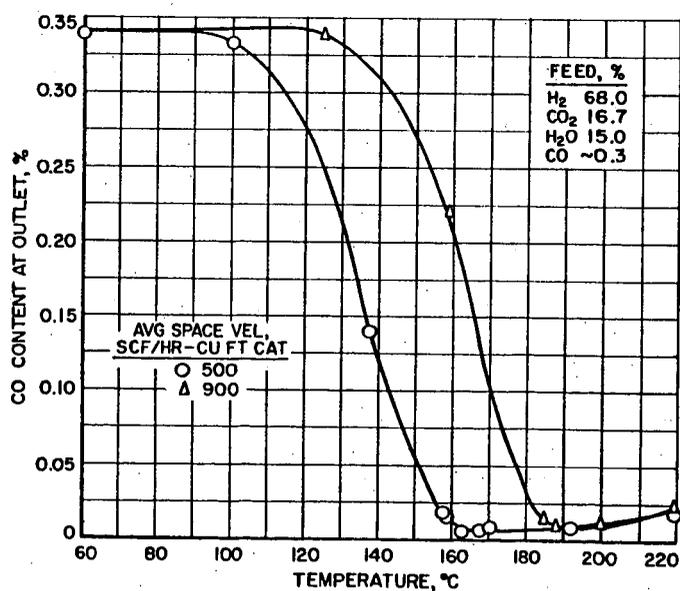


Fig. 6.-SELECTIVE METHANATION OF CARBON MONOXIDE AT HIGH WATER CONTENT

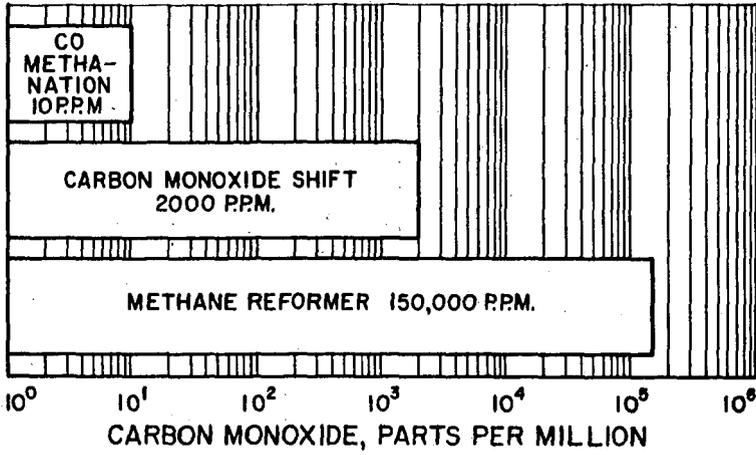


Fig. 7.-CARBON MONOXIDE REDUCTION IN IGT HYDROGEN GENERATION PROCESS

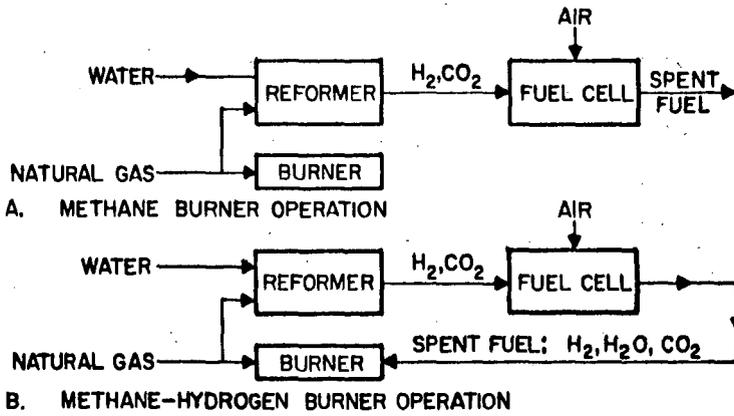


Fig. 8.-OPERATIONAL MODES FOR REFORMER-FUEL CELL-BURNER SYSTEM

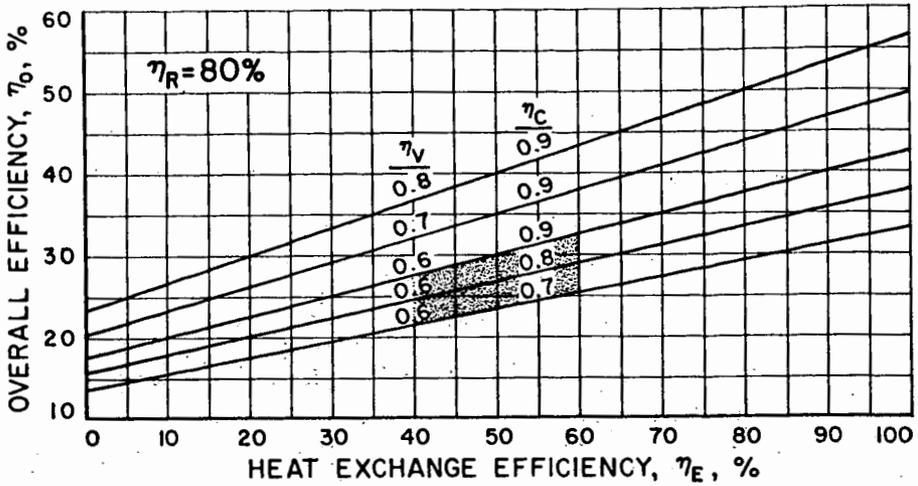


Fig. 9.-EFFECT OF FUEL CELL AND HYDROGEN GENERATOR PARAMETERS ON SYSTEM EFFICIENCY
CASE I - NO RECYCLE

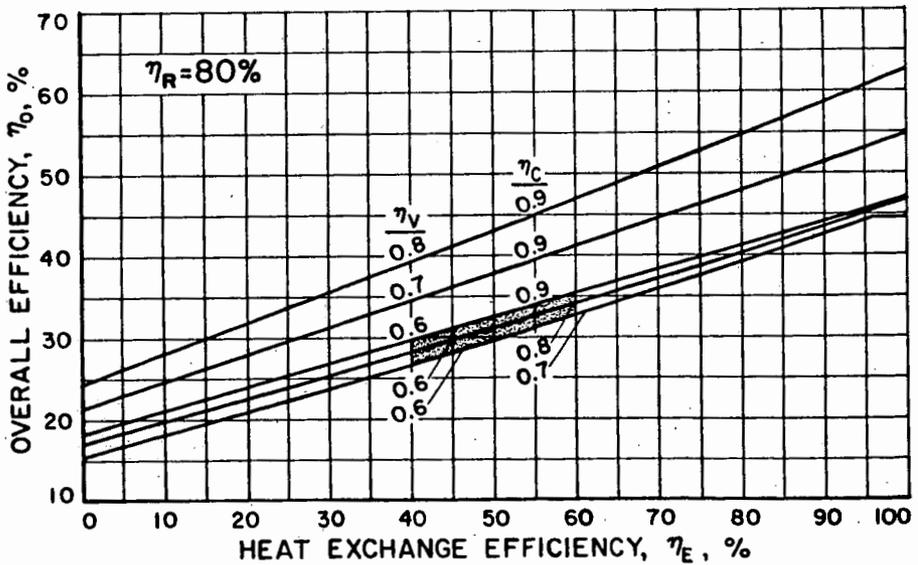


Fig. 10.-EFFECT OF FUEL CELL AND HYDROGEN GENERATOR PARAMETERS ON SYSTEM EFFICIENCY
CASE II - RECYCLE